On the hyperfine interaction in rare-earth Van Vleck paramagnets at high magnetic fields

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Abstract. An influence of high magnetic fields on hyperfine interaction in the rare-earth ions with non-magnetic ground state (Van Vleck ions) is theoretically investigated for the case of Tm^{3+} ion in axial symmetrical crystal electric field (ethylsulphate crystal). It is shown that magnetic-field induced distortions of $4f$-electron shell lead to essential changes in hyperfine magnetic field at the nucleus. The proposed theoretical model is in agreement with recent experimental data.

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1. Introduction

Van Vleck (VV) or polarization magnetism most often occurs in crystals containing non-Kramers rare-earth (RE) ions, i.e. ions with an even numbers of electrons in the unfilled $4f$-shell, where the crystalline electric field lifts the degeneracy of the ground multiplet $^{2S+1}L_J$, leading to typical splittings of the Stark structure of the order of 10-100 cm^{-1}. The electronic ground state in this case is a singlet or non-magnetic doublet so all magnetic properties of Van Vleck paramagnets are necessitated by the Zeeman effect which at moderate magnetic fields (the Zeeman energy is much more less then the Stark splittings) can be calculated in the second order of perturbation theory [1, 2, 3]. The rather strong hyperfine interaction induces the magnetic field at the nucleus of VV ion in many times greater than the applied external magnetic field and leads to enormous values (up to several hundred) of paramagnetic shift of the NMR lines. This so-called "enhanced" NMR is one the most important methods for studying the magnetic properties of VV paramagnets [2, 3].

At high magnetic fields the Zeeman energy of RE ion becomes comparable with the Stark splitting energies and a number of new physical effects appears [4]. Among them the magnetic field induced structural phase transitions in dielectric VV paramagnets $TmPO_4$ [5] and $LiTmF_4$ [6] and the coupled $4f$-electron-phonon excitations in the thulium ethylsulphate crystal $Tm(C_2H_5SO_4)_2 \cdot 9H_2O$ $(TmES)$[7] can be mentioned.

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From the theoretical point of view the applicability of perturbation theory is violated at high magnetic fields and a new theory has to be built [4, 8]. For example, it was shown in [4, 9] that at high magnetic fields the coupled $4f$-electron-nuclear states in insulating VV paramagnets appear. The resonant absorption due to the transitions between electronic-nuclear sublevels of the ground singlet in $TmES$ crystal has been observed in [10] at magnetic fields up to $3T$. It should be pointed out that the frequencies of those transitions lie almost in the X band of the EPR frequencies while the transition probabilities are determined by the matrix elements of the nuclear spin operator. From this point of view it is reasonable to speak about "ultrahigh- frequency" NMR at high magnetic field, in contrast to the "enhanced" NMR at moderate magnetic fields. The observed field dependence of transition frequencies doesn't coincide with the predicted one in [4, 9] where for clarity in setting forth the essential changes arising in properties of the nuclear-spin system of an insulating VV paramagnet under influence of a high magnetic field the possible changes in hyperfine interaction parameters were neglected. But a sufficiently high magnetic field will cause distortion of the $4f$-electron shell and a redistribution of the electron density, inevitably altering the hyperfine field at the nucleus.

In this Paper, we investigate theoretically the influence of a rather high external magnetic fields on hyperfine interaction in dielectric VV paramagnets. As a model system the well-studied at moderate magnetic fields $TmES$ crystal is considered.

2. Hyperfine interaction in VV paramagnets

The Hamiltonian of an isolated VV ion (the distance between two nearest-neighbor thulium ions in $TmES$ is ~ 7 Å and single-ion approximation works a rather well) can be written as

$$\mathcal{H} = \mathcal{H}_{cr} + \mathcal{H}_{eZ} + \mathcal{H}_{nZ} + \mathcal{H}_{hf}, \tag{1}$$

where the crystal electric field Hamiltonian in generally accepted notations [11] reads as

$$\mathcal{H}_{cr} = \alpha B_{20}O_2^0 + \beta B_{40}O_4^0 + \gamma(B_{60}O_6^0 + B_{66}O_6^6). \tag{2}$$

The Hamiltonian of the Zeeman interaction of $4f$-electron shell and that of the nuclear Zeeman interaction are in usual forms:

$$\mathcal{H}_{eZ} = g_J\mu_B\mathbf{HJ}, \mathcal{H}_{nZ} = -\gamma_I\hbar\mathbf{HI}. \tag{3}$$

The explicit form of the Hamiltonian of hyperfine interaction $\mathcal{H}_{hf}$ can be estimated in the case of RE ions in the following way (see, for example, [11]; note, that we shall not consider hereinafter quadrupole effects because of ${}^{169}Tm$ nuclear spin is one-half). For a free RE the magnetic interaction with the nucleus of the electrons in the partially filled $4f$-shell with orbital moments $\mathbf{l}_i$ and spins $\mathbf{s}_i$ is given by

$$\mathcal{H}_{hf} = 2\mu_B\gamma_I\hbar\sum_{i\in 4f}\{r_i^{-3}[\mathbf{l}_i - \mathbf{s}_i + 3\mathbf{r}_i(\mathbf{r}_i\mathbf{s}_i)/r_i^2]\}\cdot\mathbf{I} = 2\mu_B\gamma_I\hbar\langle r_i^{-3}\rangle(\mathbf{N}\cdot\mathbf{I}) \tag{4}$$

and can be represented within the the ground multiplet manifold $^{2S+1}L_J$ where the total angular momentum $\mathbf{J}$ is the good quantum number as

$$\mathcal{H}_{hf} = 2\mu_B \gamma_I \hbar \langle r_i^{-3} \rangle \langle J \| N \| J \rangle (\mathbf{J} \cdot \mathbf{I}) = A_{hf} (\mathbf{JI}). \tag{5}$$

The reduced matrix elements $\langle J \| N \| J \rangle$ are tabulated for different $4f^n$ electronic configurations [11].

For an RE ion in a crystal the crystal electric field reduces the rotational symmetry of free atom and removes partially or completely the degeneracies of energy levels. As the result there asymmetry reflected the local environment symmetry of an RE ion appears in hyperfine interaction parameter A_{hf}. So the Eq.5 has to be replaced by

$$\mathcal{H}_{hf} = (\mathbf{J} \tilde{A} \mathbf{I}). \tag{6}$$

For example, in the ethylsulphates of RE ions with magnetic ground states (electronics levels exhibit Kramer's degeneracy) the principal values of the hyperfine interaction tensor $\tilde{A}$ obtained by measurements of hyperfine structure of the paramagnetic resonance lines can differ in 10 times and more. But for VV ions, i.e. non-Kramer's ions with a non-magnetic ground state like Tm^{3+} in $TmES$ (the total angular momentum is quenched by the crystal electric field), the paramagnetic resonance is not observable and the principal values of $\tilde{A}$ are determined by indirect way. For our estimations we have used the measured by means of the enhanced NMR at moderate magnetic fields so-called paramagnetic shift [13] which is anisotropic and the values of which depend on the strength of hyperfine interaction as well as on the degree of mixing of the Stark wave functions by the applied magnetic field. Taking into account the explicit form of wave functions for the Hamiltonian $\mathcal{H}_{cr} + \mathcal{H}_{eZ}$ we get after calculations the following principal values of the hyperfine interaction tensor for Tm^{3+} in the axial crystal field in $TmES$: $A_{\|} \approx -241\,\mathrm{MHz}$ and $A_{\perp} \approx -388\,\mathrm{MHz}$ (the estimated value of A_{hf} for free tripositive ion Tm^{3+} from measurements of Tm and Tm^{2+} is -393.5 MHz [11]).

A rather high magnetic field the Zeeman energy in which is comparable with the Stark splittings of the ground multiplet leads to the further lowering of symmetry and consequently to the redistribution of $4f$-electron density in VV ions. The inclusion of a such magnetic field can be considered formally as the appearance of low-symmetry magnetic field dependent term in the crystal field Hamiltonian. Consequently we can assume that magnetic hyperfine interaction is still described by Eq.6 where the components of hyperfine interaction tensor $\tilde{A}$ depend on the strength of applied magnetic field.

Up to our knowledge *ab initio* calculations of crystal field effects and magnetic properties have not been provided for the VV paramagnets yet. So in order to estimate theoretical values of hyperfine interaction parameters in insulating VV paramagnets at high magnetic field and to compare the obtained results with the observed in [10] magnetic field dependence of the resonant frequencies due to transitions between electron-nuclear states in $TmES$ the following phenomenological model can be proposed. Assuming that the external magnetic field is not too high to destroy partially LS coupling and taking into account that hyperfine magnetic field at nucleus is determined

by the magnetic moment of $4f$-electron shell one can write for the the principal values of hyperfine interaction tensor at high magnetic field the following relation:

$$\frac{A_{\parallel,\perp}(H)}{M_{\parallel,\perp}(H)} = \frac{A_{\parallel,\perp}}{M_{\parallel,\perp}}, \tag{7}$$

where $M_{\parallel,\perp}(H)$ and $M_{\parallel,\perp}$ represents the components of the electronic magnetic moment of Tm^{3+} ion at high magnetic field and at moderate magnetic field respectively, and can be calculated by use the wave functions of the Hamiltonian $\mathcal{H}_{cr} + \mathcal{H}_{eZ}$. The principal values $A_{\parallel,\perp}$ have been determined above. Note here that because of dependence of $4f$-electron magnetic moment in VV paramagnets on the populations of the nearest excited levels (at helium temperatures) the temperature dependence of hyperfine interaction parameters is expected. The provided calculations with use above model allowed to describe the observed experimental data [10] in a good way.

3. Summary

In summary, we have showed that at rather high magnetic field the Zeeman energy of an Van Vleck ion in which is comparable with Stark structure splitting energies the components of magnetic hyperfine interaction tensor begin to be dependent on the applied magnetic field strength. The phenomenological model for taking into account the influence of the induced external magnetic field distortions of $4f$-electron shell on hyperfine magnetic field at nucleus in insulating VV paramagnets has been proposed. The results of these studies can be applied also to intermetallic VV paramagnets which are very interesting from the point of view of ultra-low temperature physics.

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